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# A New Application of Thermal Spray in Preparation of Metallic Membrane for Concentration of Glucose Solution

**M.E. Aalami-Aleagha, S.S. Madaeni, and P. Daraei**

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**Wire arc spraying has recently been used for preparation of porous metallic membranes. This work focuses on characterization of the metallic membranes produced by this technique based on porosity, oxide content, and the pore size distribution. The effect of atomizer air pressure and stand-off distance on membrane properties is examined. According to the obtained results, stronger atomizer air pressure leads to a decrease in both porosity and oxide content, while a longer stand-off distance promotes the oxide content and only increases the porosity at the distances not longer than 30 cm. A prepared metallic layer was set up in an experimental membrane cell as a permselective film for filtration of glucose solution. Generally, the water flux was appropriate, and the prepared membranes was able to remove glucose from water efficiently.**

**Keywords** glucose, metallic membrane, porosity, thermal spraying, wire arc spraying

## 1. Introduction

Thermal spray is commonly applied for depositing a protective layer over the surfaces of industrial components for increasing the resistance against corrosion, abrasive wear, and high thermal shock (Ref 1-4). Other applications also extend to production of dielectric capacitors, repairing existing parts, or even decorative arts. Recently, Kulkarni et al. (Ref 5) used this technique for producing an inorganic ceramic membrane as a catalyst in the conversion of methane into synthesis gas (i.e., a mixture of carbon monoxide and hydrogen). The ceramic membrane was produced by plasma spraying technique and used for gas separation process particularly at high temperature. Membrane is a porous or nonporous layer that is able to permeate materials selectively. Indeed, the layers produced by thermal spray technique are intrinsically porous. Hence, this technique can potentially be used to produce porous metallic and ceramic membranes.

Purification and enrichment of chemicals (raw materials and/or products) is an important part of the chemical process. Therefore, the separation process is very critical in chemical and petrochemical industries. The common methods for separation such as liquid-liquid extraction and distillation consume large amount of energy. "Membranes" have been used and developed in order to save energy and cost. The nonmetallic membrane is applied for water desalination and food processing and in some cases emerges as a unique separation process in pharmaceuticals (Ref 6). Leiknes et al. (Ref 7) have investigated the feasibility and potential of using inorganic metal microfiltration membranes with coagulation pretreatment for producing potable water. The metal membrane was also used for clarifying the rainwater due to the high treatment efficiency of microorganisms and particulates (Ref 8).

Metallic membranes can be prepared by electroplating, electroless plating, chemical vapor deposition (CVD), physical vapor deposition (PVD), and sintering processes (Ref 9). Recently, the wire arc spraying has been used for preparing porous stainless steel membrane (Ref 10). The metallic membrane can be produced in disk and tube shapes and various sizes (Ref 11).

Wire arc spraying is an inexpensive process to produce a porous structure in a short time. This technique has been used previously to produce metal layers as a membrane for purifying water (Ref 10). In the present work we have investigated the possibility of producing metallic membranes by the economic technology of arc spraying for concentration of glucose solution. The essential purpose of this study is to investigate the effect of alterations in arc spraying parameters such as stand-off distance and atomizer air pressure on prepared membrane characteristics. This is achieved by relating the pores and metal oxide in the prepared layer to the stand-off distance and atomizer air pressure for evaluating membrane performance. The filtration of glucose aqueous solution is examined using prepared membranes.

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**M.E. Aalami-Aleagha**, Department of Mechanical Engineering, Razi University, Kermanshah, Iran; and **S.S. Madaeni** and **P. Daraei**, Department of Chemical Engineering, Membrane Research Center, Razi University, Kermanshah, Iran. Contact e-mail: me_aalami_aleagha@yahoo.com.

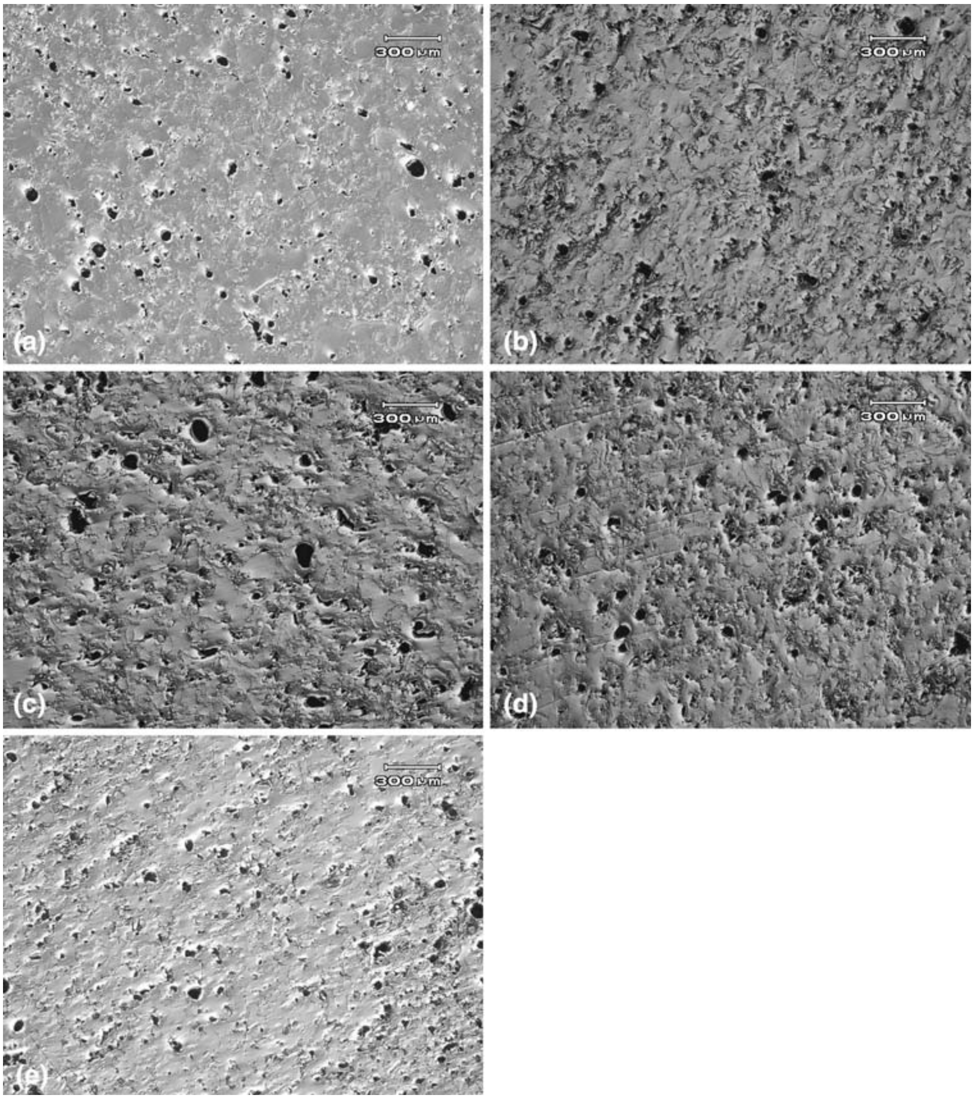

**Fig. 1** Optical microscopy images of metallic membrane prepared at various stand-off distances: (a) 15 cm, (b) 30 cm, (c) 40 cm, (d) 50 cm, (e) 65 cm

**Table 1 Spraying conditions**

| Run no. | Spray distance, cm | Atomizer air pressure, bar | Electric current, A | Wire feed, bar | Voltage, V |
|---|---|---|---|---|---|
| 1 | 15 ± 2 | 3.5 | 160 | 1.5 | 24 |
| 2 | 30 ± 2 | 3.5 | 160 | 1.5 | 24 |
| 3 | 40 ± 2 | 3.5 | 160 | 1.5 | 24 |
| 4 | 50 ± 2 | 3.5 | 160 | 1.5 | 24 |
| 5 | 65 ± 2 | 3.5 | 160 | 1.5 | 24 |
| 6 | 30 ± 2 | 3.0 | 160 | 1.5 | 24 |
| 7 | 30 ± 2 | 4.0 | 160 | 1.5 | 24 |
| 8 | 30 ± 2 | 4.5 | 160 | 1.5 | 24 |

**Table 2 Wire composition**

| Composition, wt.% | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C | Si | Mn | S | P | Cr | Ni | Mo | Cu | Fe |
| 0.15 | 1.0 | 1.0 | 0.02 | 0.03 | 12.0 | 0.8 | 0.5 | 0.75 | Balance |

## 2. Experimental Work

Spraying was carried out as specified in Table 1. The composition of the stainless steel wire used is given in Table 2. The preparation method has been explained in detail elsewhere (Ref 10). The deposited layers were picked up and used as a membrane in separation glucose from water. The membranes structure were examined using image analysis as shown in Fig. 1. The optical micrographs from as-sprayed and cross section of metal layers were captured by Olympus GX71 and DP12 camera (Olympus Co., Tokyo, Japan). The images were analyzed by Olysia m3 computer program (Olympus Co., Tokyo, Japan).

To verify the results obtained by image analysis, the coating porosity was measured using the liquid immersion technique. The deposited layers were immersed in isopropanol for 2 days without disintegrating into small pieces. Isopropanol was selected due to its low surface tension relative to water. In this way, any impurities are removed from the metal structure, and then the specimen was dried with hot air flow and weighed ($W_1$). Then the metal layer was immersed in isopropanol for 3 days. The wet specimen was moved from alcohol, and its surface was dried and weighed again ($W_2$). Ultimately, the specimen was dried by hot air flow for 30 min thoroughly, and weighed for last time ($W_3$). The value of $W_2 - W_1$ or $W_2 - W_3$ is the alcohol weight that has diffused in inner pores of metallic layer. The third weighing was performed for certainty of $W_1$. The void spaces in the membrane structure and the resulting porosity can be calculated using the weight and density of isopropanol and membrane.

The prepared membranes were set up in a dead-end membrane cell for filtration test (Fig. 2). Figure 3 demonstrates the parts of the used membrane cell in detail.

Glucose solution was made in distilled water with concentration of 100 g/L. Glucose molecules have dimensions in the nanometer range and dissolve in water molecularly. They have no interaction with any component in the water or the membrane. The water flux and glucose rejection are the important properties in membrane application and were investigated 3 h after setup. Data were obtained performed every 30 min during the test. The water flux and glucose rejection were evaluated based on:

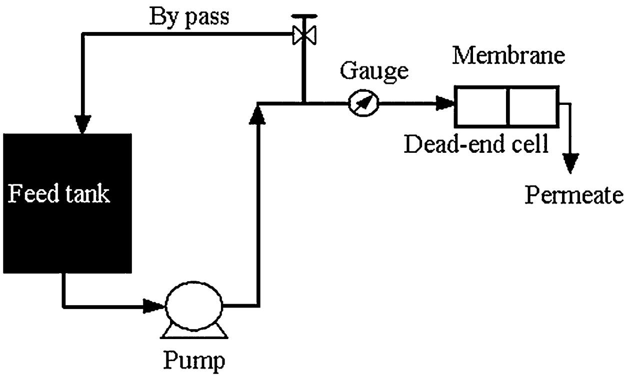

**Fig. 2** Scheme of performance test setup

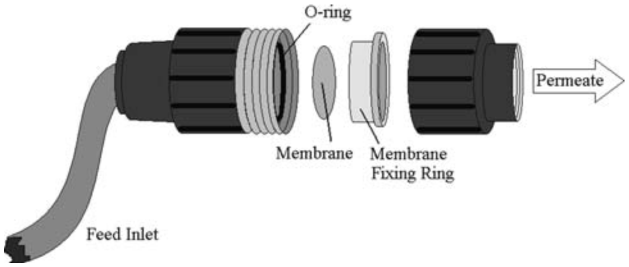

**Fig. 3** Details of dead-end membrane cell

$$\text{Water flux}\ \left(\mathrm{L/m^2\,h}\right) = \frac{V_\mathrm{p}}{At}$$

$$\text{Glucose rejection}\ (\%) = \frac{C_\mathrm{f} - C_\mathrm{p}}{C_\mathrm{f}} \times 100$$

where $V_\mathrm{p}$ is the volume of permeated water (L), $A$ is beneficial membrane surface area ($\mathrm{m}^2$), $t$ is duration time for collecting permeated water (h), $C_\mathrm{p}$ and $C_\mathrm{f}$ are the concentration of glucose in permeate and feed solution (degrees Brix, or °Br), respectively.

## 3. Results and Discussion

### 3.1 Porosity

In the current work, a metallic membrane was prepared by arc spraying process. The analysis of pores, oxide content, and pore size distribution was used to clarify the filtration capability of these metal layers. During a thermal spraying process droplets are propelled and impacted onto a solid substrate. The molten or semimolten metal droplets spread and ultimately solidify during a splatting process (Ref 12, 13). Accumulation of such splats forms a porous metal layer or metallic membrane. In the splatting process, the extent of material flow and heat-transfer rate can control the properties of the prepared layers. The pore formation can be elaborated based on three types of parameters associated with the impact process. These parameters are (i) extent of material flow and the rate of heat transfer in splatting process, (ii) target behavior and its contribution to splatting process, and (iii) the interaction between splat and target, or interface property. The first category of parameters is characterized by the splat temperature, splat velocity, splat viscosity, and surface tension of splat material. The second type of parameter, which depends on target behavior, can be evaluated by the effect of roughness, thermal conductivity, and temperature of the target. The interface property includes the wettability and the conductivity of interface during splatting process (Ref 14, 15). The architecture of pores and its morphology is also an effective parameter in associating the membrane performance of this thermal spray layers. The interconnected pores or insulated pores that are to some extent linked by networks of microcracks can increase the permeability of metal layers.

The pore in a deposited layer is formed based on unsuccessful connection of splats; this may be obtained from (a) accumulation of the irregular lamellae, (b) emerging of voids caused by the reduction of splat temperature and gas solubility in molten metal, (c) splat shrinkage during the solidification process, and (d) formation by gas bubbles or the pockets that are trapped in molten metal during atomizing process (Fig. 4). Thermal stress and/or tensile quenching stress can be enhanced the pore formation by incomplete intersplat connections or intersplat cracks (Ref 5).

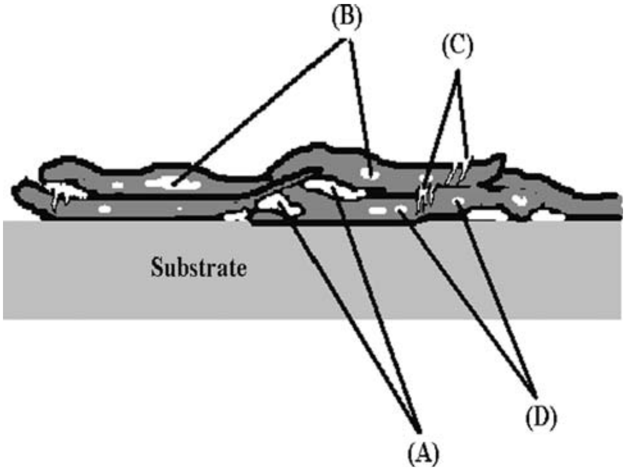

**Fig. 4** Scheme of various types of pores in sprayed layer

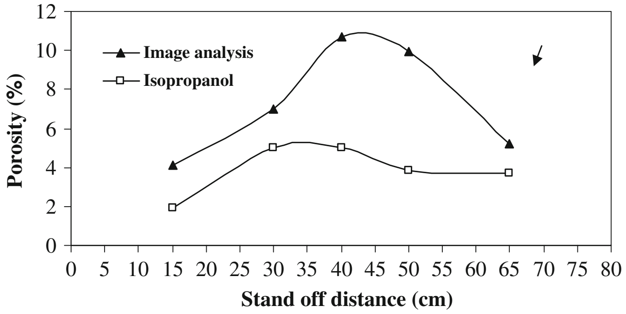

**Fig. 5** Effect of spray distance on porosity obtained by various porosity measurement methods

Splashing can also increase the pores in deposited layers. Fox and Clyne (Ref 16) have described the effect of stand-off distance on pores formation. They have used yttria-stabilized zirconia (YSZ) as a barrier layer against heat flow and unbeneficial gas permeability.

In this work, the effect of stand-off distance and atomizing air pressure on permeability was investigated. The permeability and selectivity of the produced layer was evaluated by an experimental cell.

**3.1.1 Effect of Stand-off Distance.** In Table 1, Runs 1 to 6 refer to investigation of the stand-off distance on prepared membrane properties. In a porous membrane, the main purpose is increase of the porosity as much as possible. Hence, the unusual stand-off distances, that is, distances longer than 30 cm, were also investigated. The image analysis result for pore measurement is demonstrated in Fig. 5. It shows a maximum value of porosity was obtained at a distance of ~40 cm. The captured micrographs also clearly indicate this trend (Fig. 1).

In order to confirm the results of porosity measurement and particularly for evaluating the interconnections between pores, the diffusion of isopropanol was investigated. The results indicate that both techniques verify each other (see Fig. 5). Therefore, the spray distance of ~40 cm seems to be an optimum distance for obtaining the highest porosity in metallic layers.

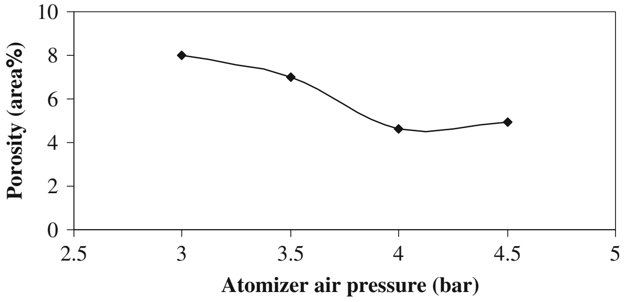

**Fig. 6** Effect of atomizer air pressure on porosity of sprayed layers

The existing porosity as indicated in Sect 3.1 refers to various sources (Fig. 4). By increasing the spray distance, metal droplets have to travel through air for a long time and type (d) pore formation mechanism or porosity source could be more active. This leads to formation of layers with more porosity. At a long stand-off distance, the temperature of molten metal droplet is reduced and partial solidification occurs. This allows splats to spread inefficiently and leads to an increase of the void spaces between splats. At distances longer than 40 cm, it seems that the oxidation on surface of the droplets is fully achieved. As the melting point of metal oxide is lower than that of the parent metal, the existing oxide remains for a long time in liquid state. Thus the molten metal oxide has a potential to move during splatting process and fill the void spaces. According to this mechanism, at long stand-off distances, that is, more than 40 cm, the porosity content in layers will ultimately be reduced (Fig. 5).

**3.1.2 Effect of Atomizer Air Pressure.** Runs 2, 7, and 8 in Table 1 were performed to evaluate the effect of atomizer air pressure on porosity of produced metal layer. An increase of atomizer air pressure decreases the porosity of the layers (Fig. 6). This may be attributed to the increase of spraying intensity, which decreases the size of molten metal droplets. By decreasing the particle size, the trapped gas in particles is declined. This results in a reduction of this type of pores in deposited layers. According to Fig. 6, between tested atomizer air pressures, three bars is the optimum atomizer air pressure for producing the highest porosity in sprayed layers.

## 3.2 Oxide Content

An effective factor on metallic membrane performance is the oxide content of prepared metal layers. This was evaluated by image analyzing of captured micrographs. The source of oxide formation in a thermal spray process has been analyzed by many researchers (Ref 17-19). This was divided into three different regions, see Fig. 7. In an arc spray process the first region is focused on the hot tip of electrodes, where the molten material is not disintegrated into the fine particles. Region II points out the free jet of spray plume, and region III encompasses the surface of recently deposited splats until it is covered by the ensuing ones. The most important region in oxide formation that is affected by the stand-off distance and

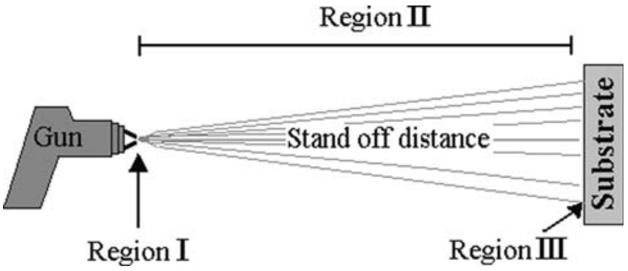

**Fig. 7** Regions for oxide formation

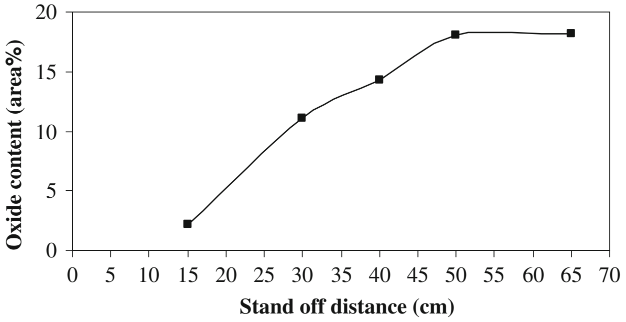

**Fig. 8** Effect of stand-off distance on oxide content of sprayed layer

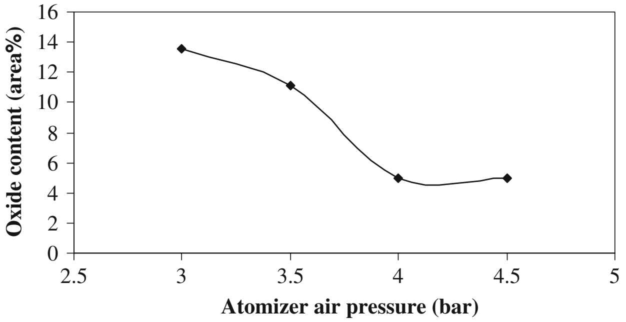

**Fig. 9** Effect of atomizer air pressure on oxide content of sprayed layer

atomizer air pressure is region II. The oxide that is formed in region II is concentrated on boundary layer of splats.

**3.2.1 Effect of Stand-off Distance.** Increasing the stand-off distance increases the residence time of particles in region II, and this provides a sufficient time for oxidizing the surface of particles (Fig. 8). A similar trend is also reported by other researchers (Ref 20, 21). Considering Fig. 8, the oxide content is not changed at stand-off distances greater than 45 cm. This may be attributed to the oxide formation over the surface of droplets. The exterior surface is covered by metal oxide and has no bare metal for oxidizing. Thus, the oxide content of sprayed layer is not promoted over the distance of 45 cm.

**3.2.2 Effect of Atomizer Air Pressure.** Increase of atomizer air pressure leads to great disintegration of the particles. Fine particles obtained high velocity in traveling through the region II. This decreases the residence time of particles in region II, which allows less time for oxide formation. Increasing the atomizer air pressure decreases the droplet temperature considerably. In this way, the oxide formation is also discouraged (see Fig. 9).

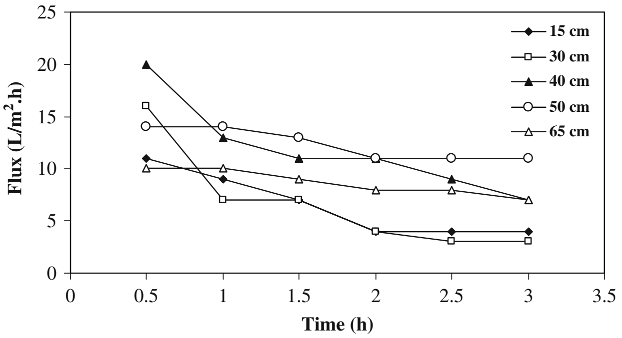

**Fig. 10** Water flux for the membrane prepared at various stand-off distances during 3 h

**Table 3 Pore size distribution in membranes prepared at various stand-off distances**

| Run no. | Spray distance, cm | Average pore size, μm | Max/min pore size, μm |
|---|---|---|---|
| 1 | 15 ± 2 | 5.95 | 127/1.33 |
| 2 | 30 ± 2 | 5.73 | 49/1.32 |
| 3 | 40 ± 2 | 6.71 | 149/1.27 |
| 4 | 50 ± 2 | 5.73 | 99/1.27 |
| 5 | 65 ± 2 | 5.32 | 104/1.27 |

### 3.3 Pore Size Distribution

Pore size was evaluated by image analysis. The results of pore size distribution are shown in Table 3. It shows that the change in stand-off distance has no noticeable effect on pore size distribution. The mean pore size at spraying distance of 40 cm becomes the largest one. Also the largest pore size is attributed to this stand-off distance.

### 3.4 Filtration Capability

According to Fig. 10, the layer that is produced at distance of 40 cm provides the highest water flux. It is the result of the high porosity. Considering Fig. 11, it can be concluded that the membrane with pores smaller than a critical pore size and low oxide content shows the highest glucose rejection (i.e., the membrane prepared at 15 cm). The capability of prepared layer in a membrane performance is defined by sufficient water flux and appropriate glucose rejection. Analyses of prepared layers elucidate that this aim can be obtained where the layers have the high porosity, small pore size, and the low oxide content.

## 4. Conclusions

In this study, wire arc spraying was used for preparing the porous metallic membrane. The results indicated that the porosity of metallic layers increases because of

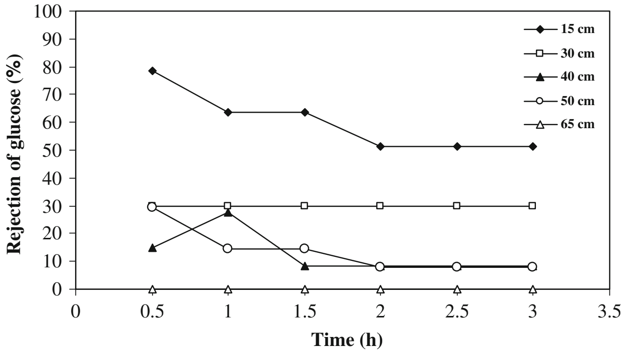

**Fig. 11** Rejection of glucose for the membrane prepared at various stand-off distances during 3 h

decreasing atomizer air pressure. However, an increase of up to 40 cm in the stand-off distance increases the porosity. The oxide content increases as a result of increasing the stand-off distance and decreasing the atomizer air pressure. This porous layer was applied as a metallic membrane to separate glucose from aqueous solution. According to the experimental results, the prepared membrane was effectively permeable to water and can remove glucose from water. The appropriate separation can be obtained by membrane with low oxide content and high porosity and fine pores lower than a critical size.

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